

Characterization of Spatial Variability Structure in Three Separate Field Trials on Pesticide Dissipation*

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Abstract: Experiments were carried out on three Italian farms to assess the degree of spatial variation of pesticide field concentration during treatment and during dissipation trials. Test pesticides were chloridazon and metamitron (both sugar-beet herbicides) applied as a tank mix. The classical statistical technique and geostatistics were used to summarize and evaluate variable spatial data.

The results show that the actual values of pesticide concentration for application rate and initial concentration in all three areas are lower than expected, thus indicating that under field conditions only a part of the pesticide reaches the soil during the distribution. The actual values for both herbicides in all three areas expressed as percentage of expected values ranged from 44.1% to 64.2% for application rate and from 40.5% to 99.5% for initial concentration. The coefficient of variation was similar for both pesticides and ranged from 23.8 to 74.1 for application rate, 24.1 and 58.8 for initial concentration and 11.1 and 110.0 for dissipation half-lives. The high variability in application rate and initial concentration could be ascribed to an uneven herbicide distribution, and in dissipation studies to variation in half-lives for the rate of herbicide loss from soil in different parts of the field.

Geostatistic analysis indicated little spatial correlation, probably because the sampling sites were widely spaced on the field. In all cases, the data were not sufficient to estimate the range of influence, probably because of the size of the experimental fields and the sampling strategy.

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1 INTRODUCTION

One of the main problems in pesticide dissipation field studies is the high variability in pesticide application and varying loss from soil in different parts of the field. Several authors¹⁻³ have reported high variability in pesticide application rate and dissipation in different experiments. Spatial variation can result from a lack of uniformity in pesticide or water application or from differences in various physical, chemical and biological processes. Spatial variation in the pesticide application rate and the initial soil pesticide concentration was found both in carefully prepared small-scale experiments and in large plot experiments. In dissipation studies this variability of pesticide concentration also increases, owing to the influence of various physical, chemical and biological processes.

The aims of this study were to assess the impact of spatial variation of pesticide concentration in three experimental areas with different pedoclimatic conditions but similar agronomic practices, during treatment and during dissipation trials. Test pesticides were chloridazon and metamitron, both sugar-beet herbicides. Two general approaches were used to summarize and evaluate variable spatial data: the classical statistical technique and geostatistics.

The regionalized variable theory (geostatistics) has been used in many cases to analyse the spatial variability of some physical and chemical properties of soil,⁴⁻⁶ but only in very few cases^{7,8} has this theory been

applied to spatial variability of pesticide concentration in field soils.

The geostatistic approach provides information about the variability of the observations with respect to the coordinates of the area being sampled and, while considering the coordinate position of the individual measurements, it does not depend upon a knowledge of a theoretical frequency distribution as is the case with analyses based upon the classical statistical technique.⁹ A possible use of geostatistics is the characterization of the structure of spatial variability in order to establish experimental design for further trials on pesticide dissipation studies (number of samples that should be taken as a function of the variability and the size of the field). Another possible use of geostatistics is the mapping of the field variability using kriging⁵ but this is beyond the scope of this paper. Geostatistical technique will be discussed in this paper with reference to its influence upon experimental design as well as data collection, analysis and interpretation.

2 MATERIALS AND METHODS

2.1 Layout of the experiments

Experiments were carried out on three farms located in Piacenza (northern Italy, 51 m above sea level, 45°N, silty clay loam soil); Perugia (central Italy; 155 m above sea level, 42°N, silt loam soil) and Rome (central Italy; 105 m above sea level, 42°N, clay loam soil) with nine

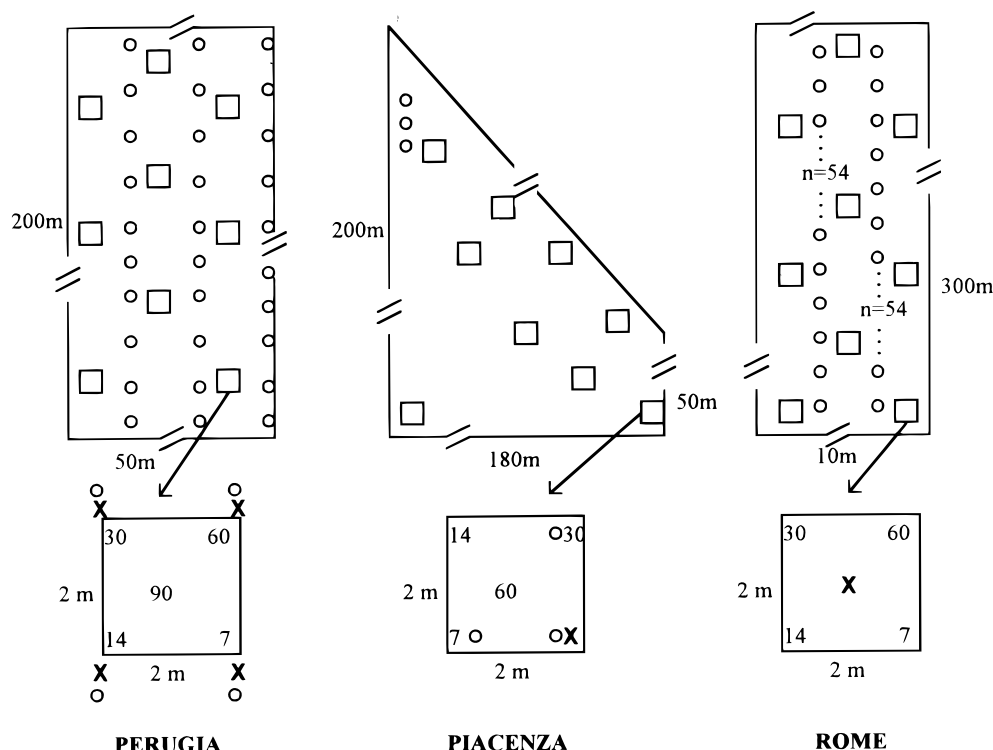


Fig. 1. Layout of the experiments (O = application rate sample sites; X = initial concentration sample sites; 7, 14, 30, 60 and 90 = dissipation sample sites; numbers refer to days after pesticide application).

4-m² sampling plots within large experimental fields of 2, 1 and 0.3 ha, respectively, as shown in Fig. 1. Sugar-beet was cultivated following the standard agronomic practices used on each farm. Metamitron and chloridazon were applied as a tank mix pre-emergence using a tractor-mounted sprayer (similar sprayers were used in the three experimental areas; they had a 10 m boom, and brass cone-nozzles 50 cm apart). Application rates, treatment dates, soil properties and climatic conditions during the experimental trials are given in Table 1. Soil samples were taken from fixed sites in each plot as follows (Fig. 1):

—application rate samples: glass boxes of 70 cm² area (30 from Piacenza in nine rows, 66 from Perugia in six rows and 108 from Rome in a single row) (one row = one sprayer pass)

—initial concentration samples: soil cores 5 cm deep × 50 cm² area (nine from Piacenza and Rome and 36 from Perugia)

—dissipation study samples: soil cores from 30 to 100 cm deep × 50 cm² area divided into 10-cm layers taken at different times from treatment (nine from each area and at each sampling time). Sugar-beet was cultivated following the standard agronomic practices used on each farm.

2.2 Herbicide extraction and analysis

Herbicide analyses were carried out following the method of Ghebbioni and Trevisan.¹⁰ This involves extraction with acetone followed by HPLC on an RP-18 column using methanol + water as mobile phase.

2.3 Statistical techniques

2.3.1 Classical

Data collected in the three fields were subjected to analysis of variance by using the GLM procedure of SAS.¹¹ A preliminary analysis had shown that no transformations were needed to meet the distribution assumptions for ANOVA.

Total data variability was divided into three main effects: between fields, between rows (nested within fields) and within row. *F* tests were used to assess whether the first two (fields and rows) could be considered to affect data variability significantly.

2.3.2 Geostatistics

The GeoEAS program¹² was used for geostatistic analyses. The program calculates the semivariance $\gamma(h)$

TABLE 1
Field Information

Soil properties								
Site	Depth (cm)	pH (H ₂ O)	Organic matter (%)	Clay (%)	Silt (%)	Sand (%)	Bulk density (kg litre ⁻¹)	CaCO ₃ (%)
Perugia	0–30	8.2	1.78	26.4	55.2	18.4	1.35	28.0
	30–50	8.2	1.77	27.6	54.3	18.1	1.35	27.7
Piacenza	0–20	7.8	2.21	35.7	47.2	17.0	1.60	9.6
	20–40	7.8	2.14	33.8	49.5	16.7	1.40	10.0
Rome	0–30	7.4	1.44	38.3	20.0	41.7	1.40	6.4
	30–50	7.4	1.50	38.0	21.0	41.0	1.35	6.1
Agronomic information								
Site	Treatment date	Rate of application (kg ha ⁻¹)		Rainfall (mm)	Absolute min. temp. (°C)	Absolute max. temp. (°C)		
		Metamitron	Chloridazon					
Perugia	10 March	2.6	2.0					
Piacenza	03 March	2.2	2.1					
Rome	23 March	2.0	1.9					
Climatic conditions during the experimental trials								
Site	Mean min. temp. (°C)	Mean max temp. (°C)	Rainfall (mm)	Absolute min. temp. (°C)	Absolute max. temp. (°C)			
Perugia	4.5	19.0	83.4	–2.9	25.2			
Piacenza	2.1	15.2	61.1	–3.0	28.8			
Rome	5.8	21.4	114.6	3.0	31.8			

as follows:

$$\gamma(h) = 1/[2N(h)] \cdot \sum_{i=1}^N [z(i) - z(i+h)]^2$$

where $N(h)$ is the number of pairs $(z(i), z(i+h))$ of samples that are separated by a lag distance of h .

A plot of γ versus h is called a semivariogram. Although, by definition, $\gamma(h) = 0$ when $h = 0$, it is often found in practice^{13–15} that as h approaches 0, $\gamma(h)$

approaches a positive finite value, which is commonly called the nugget effect, C_0 . As h increases, $\gamma(h)$ often increases up to some value, say a , after which it remains approximately constant. The plateau value of $\gamma(h)$ at this point, referred to as the sill C , is equal to the total variance of the data and the distance a is called the range and represents the separation distance beyond which the parameter values are unrelated, that is, spatially independent. When the semivariogram shows complete discontinuity at the origin, then $\gamma(h) = C$,

TABLE 2
Mean, Standard Deviation (SD), and Coefficient of Variation (CV) of Metamitron and Chloridazon Concentration for Application Rate, Initial Concentration and Dissipation Half-Lives

<i>Application rate</i>					
<i>Pesticide</i>	<i>Site</i>	<i>n^a</i>	<i>Mean (kg ha⁻¹)</i>	<i>SD</i>	<i>CV (%)</i>
Metamitron	Perugia	66	1.37	1.01	73.7
	Piacenza	30	0.97	0.42	44.0
	Rome	108	0.98	0.23	23.8
Chloridazon	Perugia	66	1.10	0.81	74.1
	Piacenza	30	1.01	0.36	35.7
	Rome	108	1.22	0.31	25.8
<i>Initial concentration</i>					
Metamitron	Perugia	36	2.20	1.13	51.2
	Piacenza	9	1.42	0.70	49.5
	Rome	9	0.81	0.19	24.1
Chloridazon	Perugia	36	1.99	1.17	58.8
	Piacenza	9	1.48	0.71	48.0
	Rome	9	1.21	0.37	30.7
<i>Dissipation studies</i>					
<i>Mean (DT₅₀)</i>					
Metamitron	Perugia	9	25.5	10.5	41.2
	Piacenza	9	26.8	9.7	36.0
	Rome	9	20.0	2.2	11.1
Chloridazon	Perugia	9	113.0	125.0	110.0
	Piacenza	9	22.2	7.4	33.2
	Rome	9	49.2	10.9	22.1

^a Number of samples

TABLE 3
Analysis of Variance for Application Rate

<i>Pesticide</i>		<i>Degrees of freedom</i>	<i>Sum of squares</i>	<i>Main square</i>	<i>F</i>	<i>P</i>
Metamitron	Between fields	2	29969	14984	19.61	<0.01
	Between rows	13	45642	3510	4.59	<0.01
	Within rows	188	143695	764		
	Total	203				
Chloridazon	Between fields	2	27720	13860	18.56	<0.01
	Between rows	13	22184	1706	2.29	<0.01
	Within rows	188	140380	746		
	Total	203				

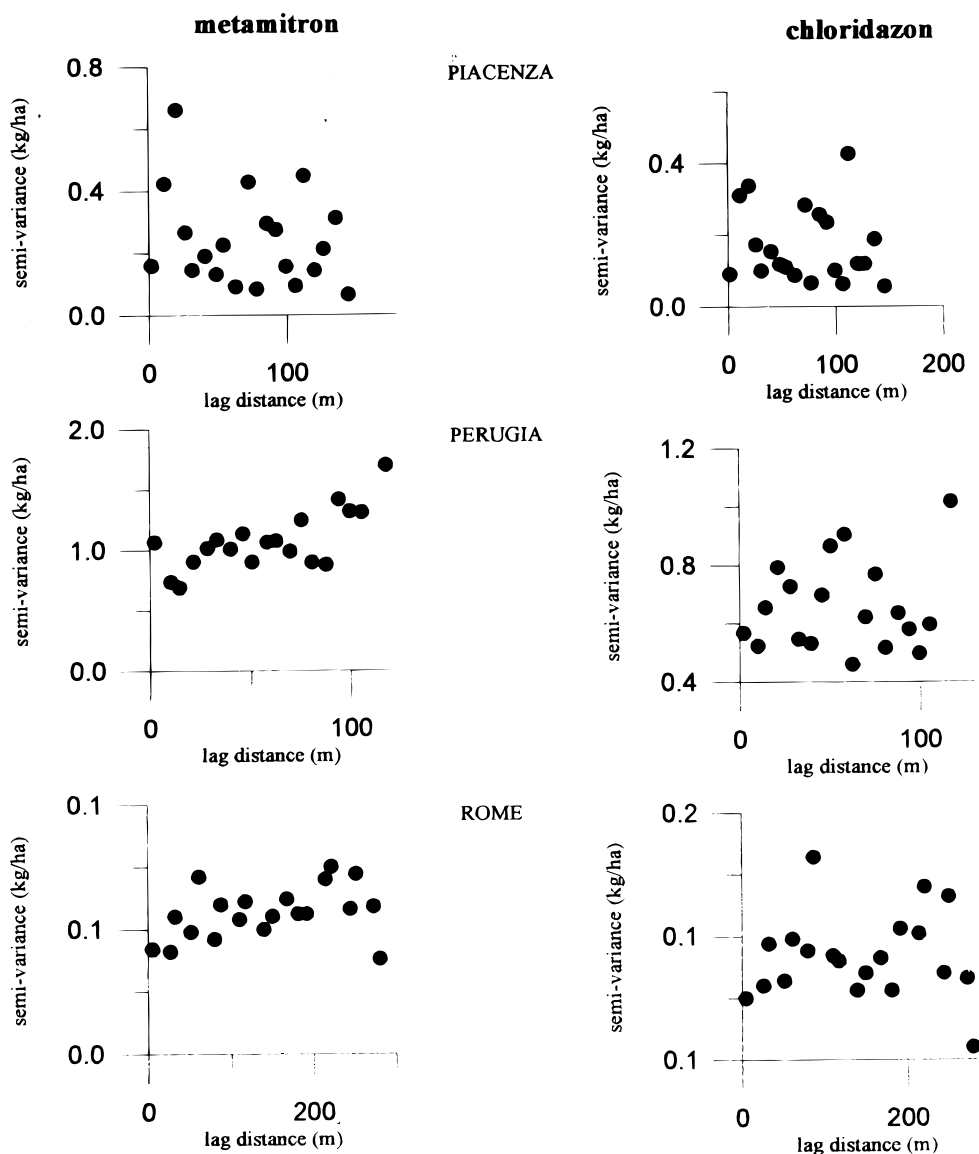


Fig. 2. Semivariograms all directions for initial concentration.

($h > \epsilon$). Where ϵ is smaller than the spacing of the experimental values, we have a pure nugget effect which corresponds to a total lack of structure on the spacing measured.

3 RESULTS AND DISCUSSION

Table 2 shows the mean, the standard deviation and the coefficient of variation for the three sites and for the application rate, initial concentration and dissipation half-lives, including all sampling times and all depths (DT_{50} = time in days for 50% of field loss). The relatively high values of the statistical parameters are in agreement with other reports.^{3,8} The actual values of pesticide concentration for application rate and initial concentration in all three areas are lower than expected, indicating that, in the practical situation, only a part of the pesticide reaches the soil during the distribution.

Analysis of variance performed only for application rate data (Table 3) showed that the overall variability of the data can be divided into the three different components: between fields, between rows (intended as passages of the sprayer) within the same field and within rows. Each of these components significantly influences the initial concentration value of the two pesticides.

The above findings are most likely to be due to the type of treatment carried out in the fields and to the climatic conditions during the day of application. The size of the field in the Rome trial was such that one pass with the sprayer sufficed to distribute the pesticides throughout the whole field. However, the larger fields at Piacenza and Perugia required 18 and six passes, respectively, so that there may have been some overlapping of spray distribution.

A previous study,¹⁶ using spray traps to evaluate the application rate, reported actual versus expected values as being 99 and 96% for chloridazon and metamitron,

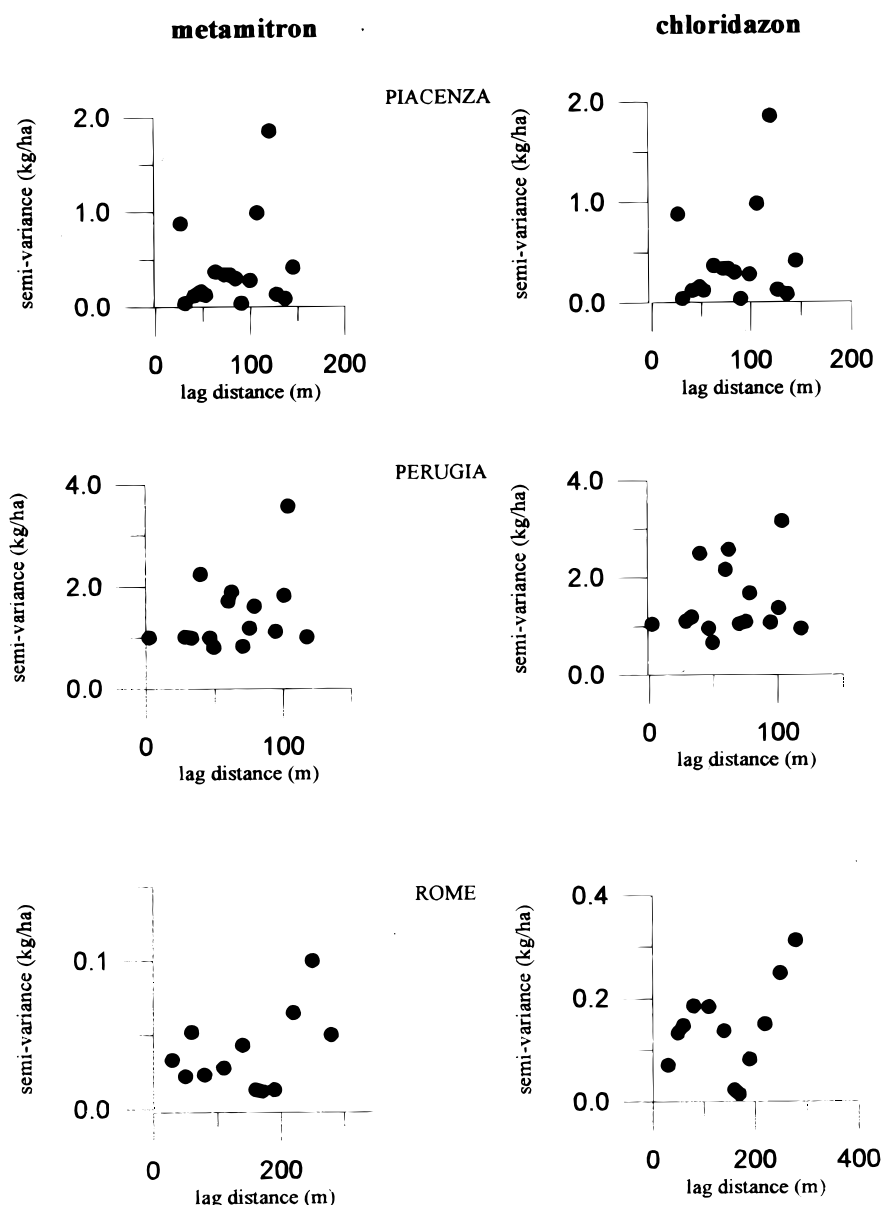


Fig. 3. Semivariograms all directions for application rate.

respectively. Since photolysis and degradation cannot have been the cause of the low concentrations measured in soil and traps in the present experiment, it could be reasonably attributed to spray drift (wind speeds at the time of treatment were 6, 4 and 4 m sec⁻¹ in the Piacenza, Perugia and Rome areas, respectively), which reduced the sampling efficiency of the spray traps and enhanced overall variability. However, it is difficult to explain the higher and unexpected concentrations measured in soil compared to spray traps in the Piacenza and Perugia areas. The different position in the field of the traps to the soil sampling points, together with the fact that spray traps were removed soon after each pass, might have affected the amount sampled and measured.

The high variability in dissipation studies could be partly ascribed to the variation in the rate of herbicide loss from soil in different parts of the field. This is a

direct consequence of the uneven distribution and, above all, of coarse soil tillages which can allow the formation of soil fissures and preferential water flows and a subsequent highly irregular distribution of pesticides through the soil profile. Furthermore, variability between fields in dissipation studies could be due to differences in soil characteristics and climatic conditions in the three areas, consequently affecting degradation, volatilization and mobility of the two pesticides. Degradation of the two pesticides is enhanced by soil temperature and moisture,^{16,17} and reduced when they are present simultaneously.¹⁸ Volatilization does not seem to affect dissipation, as shown by K_H values (both less than 10⁻¹⁰).¹⁹ Mobility is affected by soil sorption and water percolation. Laboratory measurements¹⁷ have shown that sorption of metamitron in the three soils varies considerably (Rome five times and Perugia twice

that at Piacenza), probably due to the different amounts of organic carbon, clay and calcium carbonate present in the soils. Percolated water also varies in the three fields¹⁷ and this may be due to differing field capacity and conductivity, as well as to the different size and distribution of the aggregated clods in the three fields.

To assess any possible spatial correlation, semivariograms for all directions were produced for the application rate and initial concentration. The results, summarized in Figs 2 and 3, show very little spatial correlation, probably because the sampling sites were widely spaced on the field. Only the data concerning the metamitron application rate in the Perugia area show a slightly increasing trend of semivariance (from 0.74 at 10 m to 1.6 at 118 m) thus indicating a spatial correlation of values over the entire range of distances. In all cases, the data were not sufficient to estimate the range of influence, probably because of the size of the experimental fields and the sampling strategy. These situ-

ations fall within the case of $\gamma(h) = C$ with a pure nugget effect which corresponds to a total lack of structure of variability. The sill values are consistent with the classical statistical parameters, so that the lowest semivariance values are those of the Rome area.

Semivariance values were also used to determine whether the concentrations of the two pesticides were spatially correlated, since they were applied as a tank mix. Figure 4 compares the semivariances of the two pesticides in the three areas as regards application rate and initial concentration. The correlation is significant in all cases ($P < 0.001$), except for the application rate in the Perugia area. This could be explained by the lack of pressure at the nozzles at the beginning of passing. Indeed in the first row of the spray traps, concentration values of the two pesticides are not correlated at all. The correlation test performed omitting the data for the first row of spray traps, gives $R^2 = 0.444$ ($P < 0.001$), which supports the above explanation.

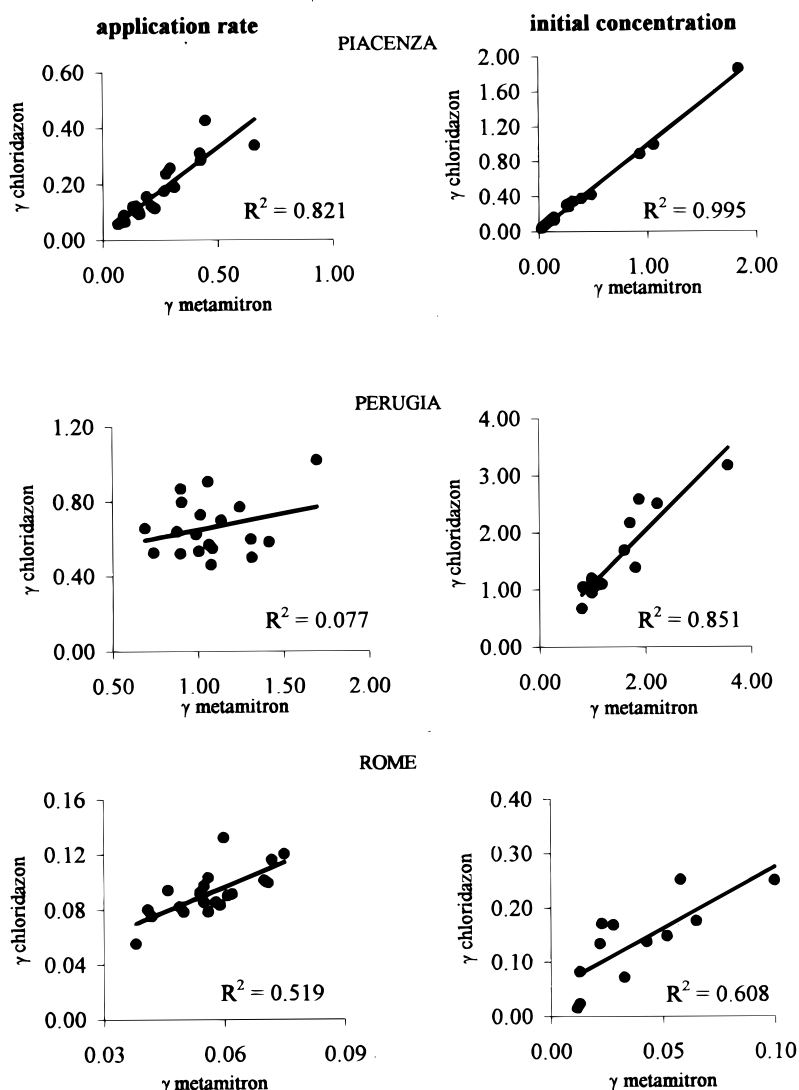


Fig. 4. Semivariance (γ) correlation, at the same lag distance, of the two pesticides in the three areas as regards application rate and initial concentration.

4 CONCLUSIONS

The experiment performed confirms the high data variability in pesticide dissipation field studies when they are carried out in agricultural conditions without standard operating procedures.

The characterization of spatial variability in field conditions allows the actual extent of possible variation in pesticide application to be determined and offers a reliable tool for model simulations of pesticide soil fate in areas of any size, provided the same agricultural practices are performed.

The variability between fields with slightly different soil characteristics shows that climatic conditions and their relation with local soil characteristics greatly influence pesticide dissipation. This should be taken into consideration when defining scenarios for registration processes or for constructing pesticide contamination vulnerability maps.

REFERENCES

1. Fryer, J. D. & Kirkland, K., Field experiments to investigate long-term effects of repeated applications of MCPA, tri-allate, simazine and linuron: report after 6 years. *Weed Res.*, **10** (1970) 133–58.
2. Wauchope, R. D., Chandler, J. M. & Savage, K. E., Soil sample variation and herbicide incorporation uniformity. *Weed Sci.*, **25** (1977) 193–6.
3. Walker, A. & Brown, P. A., Spatial variability in herbicide degradation rates and residues in soil. *Crop Prot.*, **2**(1) (1983) 17–25.
4. Webster, R. & Burgess, T. M., Optimal interpolation and isarithmic mapping of soil properties. I. The semi-variogram and punctual kriging. *J. Soil Sci.*, **37** (1980) 315–31.
5. Vieira, S. R., Nielsen, D. R. & Biggar, J. M., Spatial variability of field-measured infiltration rate. *Soil Sci. Soc. Am. J.*, **45** (1981) 1040–8.
6. Russo, D. & Bresler, E., Soil hydraulic properties as stochastic processes: II. Errors of estimates in a heterogeneous field, *Soil Sci. Soc. Am. J.*, **46** (1982) 20–6.
7. Rao, P. S. C. & Wagenet, R. J., Spatial variability of pesticides in field soils: methods for data analysis and consequences, *Weed Sci.*, **33**(Suppl. 2) (1985) 18–24.
8. Smith, C. N. & Parrish, R. S., A field study to evaluate leaching of aldicarb, metolachlor and bromide in a sandy loam soil, *J. Environ. Qual.*, **22** (1993) 562–77.
9. Fisher, R. A., *Statistical Methods and Scientific Inference*. Oliver and Boyd, Edinburgh, 1956.
10. Ghebbioni, C. & Trevisan, M., Determination of sugar-beet herbicides in soil samples. *Pestic. Sci.*, **34** (1992) 105–7.
11. SAS Institute Inc. *Introductory Guide for Personal Computers. Release 6.03*, SAS Institute, Cary, NC, USA, 1988.
12. *Geo-EAS, Release 1.2.1*. US EPA, Environmental Monitoring System Laboratory, Las Vegas, NV, USA, 1990.
13. Delhomme, J. P., *Kriging in hydrosciences*. Centre D'Informatique Geologique, Fontainebleau, France, 1976.
14. Campbell, J. B., Spatial variation of sand content and pH within single contiguous delineation of two soil mapping units. *Soil Sci. Soc. Am. J.*, **42** (1978) 460–4.
15. Burgess, T. M. & Webster R., Optimal interpolation and isarithmic mapping of soil properties: I. The semi-variogram and punctual kriging. *Soil Sci.*, **31** (1980) 315–31.
16. Capri, E., Ghebbioni, C. & Trevisan, M., Metamitron and chloridazon dissipation in a silty clay loam soil. *J. Agric. Food Chem.*, **43** (1995) 247–53.
17. Trevisan, M., Capri, E., Del Re, A. A. M., Vischetti, C., Marini, M., Businelli, M., Donnarumma, L., Conte, E. & Imbroglini, G., Evaluation of pesticide leaching models with three Italian data sets. In *Pesticide Movement to Water*, ed. A. Walker, S. W. Bailey, A. M. Blair, C. D. Brown, P. Guenther, C. R. Leake & P. H. Nicholls. BCPC Monograph 62, The British Crop Protection Council, Farnham, Surrey, 1995, pp. 269–74.
18. Vischetti, C., Marini, M., Businelli, M. & Onofri, A., The effect of temperature and coapplied herbicides on the degradation rate of phenmedipham, chloridazon and metamitron in a clay loam soil in the laboratory. In *The Environmental Fate of Xenobiotics*, ed. A. A. M. Del Re, E. Capri, S. P. Evans & M. Trevisan. Edizioni La Goliardica, Pavese, 1996, pp. 287–94.
19. Nicholls, P. H., Physicochemical evaluation: The environment, an expert system for pesticide registration assessment. *Proc. Brighton Crop Prot. Conf.—Pests and Diseases*, 1994. British Crop Protection Council, Farnham, Surrey, 1994, pp. 1337–43.